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**AS ORIGINALLY FILED****High-functionality, highly branched polyureas**

## Description

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The present invention relates to specifically synthesized high-functionality highly branched polyureas based on ureas and polyamines and to a process for preparing them.

10 The high-functionality highly branched polyureas of the invention can be used for instance as adhesion promoters, thixotropic agents, solubilizers, surface modifiers or as building blocks for preparing polyaddition or polycondensation polymers, for example for preparing paints and varnishes, coatings, adhesives, sealants, corrosion inhibitors, castable elastomers or foams.

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Polyureas are customarily obtained by reacting isocyanates with water or isocyanates with amines. The reactions are very exothermic and products are obtained which are nonuniform and have a high degree of crosslinking. Consequently polyureas are generally insoluble in known organic solvents. On this point see also Becker/Braun, 20 Kunststoff-Handbuch Volume 7, Polyurethane, Hanser-Verlag 1993.

High-functionality polymers of defined construction which contain urea groups are known.

25 WO 98/52995 describes dendrimeric highly branched polyurethane polyols which can be prepared using isocyanates having a primary and a tertiary NCO group and dialkanolamines by means of a shell-type (generational) synthesis. The synthesis produces urea urethanes with a distinct preponderance of urethane groups in the molecule (ratio of urea groups to urethane groups 1:2).

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EP-A-1 026 185 describes the preparation of highly branched polyurethane polyols which without employing protecting group techniques are prepared by specific synthesis by means of AB<sub>2</sub> and AB<sub>3</sub> structures, utilizing intramolecular differences in

reactivity among the reactants. The reaction is terminated by adding one of the two reactants in excess. Here too use is made of amino alcohols, and again urethane groups are dominant among the linking groups (ratio of urea groups to urethane groups = 1:2 or 1:3).

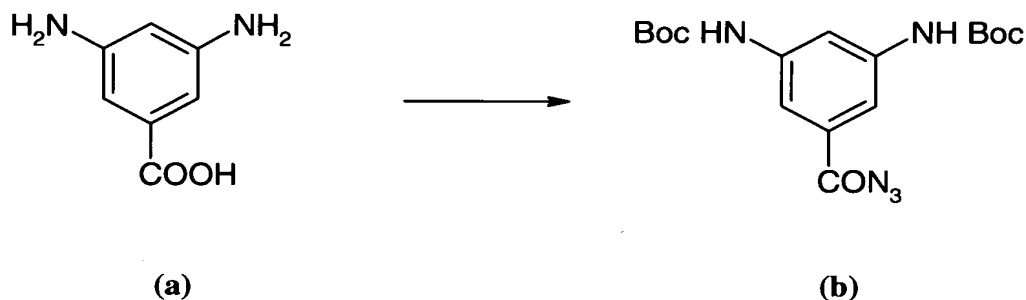
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DE-A-100 30 869 describes the preparation of polyfunctional polyisocyanate polyaddition products for which isocyanate-reactive components specified include amino alcohols and diamines and triamines as urea formers. The amines are used in conjunction with alcohols, since the reaction of diisocyanates with diamines or triamines alone, owing to its exothermic nature, is difficult to control.

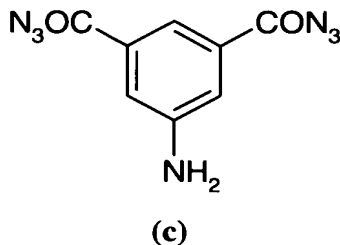
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High-functionality hyperbranched polyureas are described by A. Kumar and E.W. Meijer, Chem. Commun. 1629 (1998), and by the same authors in Polym. Prep. 39, (2), 619 (1998). The products described therein are prepared from 3,5-diaminobenzoic acid (a), which over a number of reaction steps is converted into the amine-blocked carboxylic azide (b). Subsequently the protecting groups are eliminated and the 3,5-diaminobenzoyl azide is heated to form a polyurea, with elimination of nitrogen. The products are described in the cited publications as being extremely difficult to dissolve.

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25 A. V. Ambade and A. Kumar, J. Polym. Sci. Part A, Polym. Chem. 39, 1295 – 1304 (2001) describe high-functionality highly branched polyureas which are prepared analogously from 3,5-diaminobenzoyl azide or from 5-aminoisophthaloyl azide (c).



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The products obtained are likewise described by the authors as being insoluble in all customary solvents.

5 The azide route for preparing polyureas is unattractive not least from a technical standpoint, owing to the following considerations:

- the multistage synthesis employing protecting group techniques gives rise to high production costs;
- owing to the azide reactivity only aromatic urea products can be prepared;
- handling of aromatic carboxylic azides or aromatic amines on a large scale is objectionable on safety grounds.

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High-functionality hyperbranched aliphatic polyureas can also be prepared in accordance with WO 98/50453 or with S. Rannard and N. Davis, Polym. Mat. Sci. Eng. 84, 2 (2001). According to the process described therein triamines having three primary or two primary and one secondary amine functions, e.g., trisaminoethylamine or dipropylenetriamine, are reacted with carbonyldiimidazole as a phosgene analog compound. The initial products are imidazolides, which then react further intermolecularly to form the polyureas. The disadvantage of this synthesis is on the one hand the comparatively high price of carbonyldiimidazole and on the other the fact that the resultant products always contain terminal imidazolid groups, which are labile and have to be converted into urea groups in a hydrolysis step.

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US 2002/0161113 A1 describes the preparation of hyperbranched polyureas by reacting polyamines with polyisocyanates. The reactants are combined at a temperature of  $-78^{\circ}\text{C}$ . This process is very complex for production of the products on the industrial scale.

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The object underlying the invention was therefore to provide aliphatic and aromatic high-functionality highly branched polyureas whose structures are readily adaptable to the requirements of the application and which on the basis of their defined structure have advantageous properties, such as high functionality, high reactivity, and effective solubility, and also to provide an easily implemented process for preparing the high-functionality highly branched polyureas.

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This object is achieved through a process for preparing high-functionality highly branched polyureas which involves reacting one or more ureas with one or more amines having at least two primary and/or secondary amino groups, at least one amine  
5 having at least three primary and/or secondary amino groups.

The invention also provides the polyureas thus prepared themselves.

Suitable ureas are urea and also ureas with aliphatic, aromatic or mixed  
10 aliphatic/aromatic substitution, preference being given to urea, thiourea or aliphatically substituted ureas or thioureas with linear, branched or cyclic C<sub>1</sub>-C<sub>12</sub> alkyl radicals. Examples are ethyleneurea, 1,2- or 1.3-propyleneurea, N,N'-diphenylurea, N,N'-ditolylurea, N,N'-dinaphthylurea, N-methyl-N'-phenylurea, N-ethyl-N'-phenylurea, N,N'-dibenzylurea, N,N'-dimethylurea, N,N'-diethylurea, N,N'-dipropylurea, N,N'-dibutylurea,  
15 N,N'-diisobutylurea, N,N'-dipentylurea, N,N'-dihexylurea, N,N'-diheptylurea, N,N'-dioctylurea, N,N'-didecylurea, N,N'-didodecylurea, carbonylbiscaprolactam, ethylenethiourea, propylenethiourea, N-methylthiourea, N-ethylthiourea, N-propylthiourea, N-butylthiourea, N-phenylthiourea, N-benzylthiourea, N,N'-dimethylthiourea, N,N'-diethylthiourea, N,N'-dipropylthiourea, N,N'-dibutylthiourea,  
20 N,N,N',N'-tetramethylthiourea, N,N,N',N'-tetraethylthiourea, thiocarbonyldiimidazole and thiocarbonylbiscaprolactam. Particular preference is given to urea, thiourea, N,N'-dimethylurea, N,N'-diethylurea, N,N'-dibutylurea, N,N'-diisobutylurea and N,N,N',N'-tetramethylurea.

25 Urea can be prepared for example by reacting ammonia with carbon dioxide or with phosgene. Substituted ureas can be obtained by reacting phosgene with alkylamines or arylamines or by transamidating urea with monosubstituted amines. Thiourea is obtained by reacting calcium cyanamide with hydrogen disulfide. Further methods of preparing ureas and thioureas are described for example in Ullmann's Encyclopedia of  
30 Industrial Chemistry, 6th Edition, 2000 Electronic Release, Wiley-VCH.

In accordance with the invention the ureas are reacted with one or more amines having at least two primary and/or secondary amino groups, at least one amine having at least three primary and/or secondary amino groups. Amines having two primary and/or  
35 secondary amino groups produce a chain extension within the polyureas, whereas amines having three or more primary or secondary amino groups are responsible for the branching in the resultant high-functionality, highly branched polyureas.

Suitable amines having two primary or secondary amino groups which are reactive toward a urea group are for example ethylenediamine, N-alkylethylenediamine, propylenediamine, 2,2-dimethyl-1,3-propylenediamine, N-alkylpropylenediamine, butylenediamine, N-alkylbutylenediamine, pentanediamine, hexamethylenediamine, N-alkylhexamethylenediamine, heptanediamine, octanediamine, nonanediamine, decanediamine, dodecanediamine, hexadecanediamine, tolylenediamine, xylylenediamine, diaminodiphenylmethane, diaminodicyclohexylmethane, phenylenediamine, cyclohexylenediamine, bis(aminomethyl)cyclohexane, diaminodiphenyl sulfone, isophoronediamine, 2-butyl-2-ethyl-1,5-pentamethylenediamine, 2,2,4- or 2,4,4-trimethyl-1,6-hexamethylenediamine, 2-aminopropylcyclohexylamine, 3(4)-aminomethyl-1-methylcyclohexylamine, 1,4-diamino-4-methylpentane, amine-terminated polyoxyalkylene polyols (known as Jeffamines) or amine-terminated polytetramethylene glycols.

The amines preferably have two primary amino groups, such as, for example, ethylenediamine, propylenediamine, 2,2-dimethyl-1,3-propanediamine, butylenediamine, pentanediamine, hexamethylenediamine, heptanediamine, octanediamine, nonanediamine, decanediamine, dodecanediamine, hexadecanediamine, tolylenediamine, xylylenediamine, diaminodiphenylmethane, diaminodicyclohexylmethane, phenylenediamine, cyclohexylenediamine, diaminodiphenyl sulfone, isophoronediamine, bis(aminomethyl)cyclohexane, 2-butyl-2-ethyl-1,5-pentamethylenediamine, 2,2,4- or 2,4,4-trimethyl-1,6-hexamethylenediamine, 2-aminopropylcyclohexylamine, 3(4)-aminomethyl-1-methylcyclohexylamine, 1,4-diamino-4-methylpentane, amine-terminated polyoxyalkylene polyols (Jeffamines) or amine-terminated polytetramethylene glycols.

Particular preference is given to butylenediamine, pentanediamine, hexamethylenediamine, tolylenediamine, xylylenediamine, diaminodiphenylmethane, diaminodicyclohexylmethane, phenylenediamine, cyclohexylenediamine, diaminodiphenyl sulfone, isophoronediamine, bis(aminomethyl)cyclohexane, amine-terminated polyoxyalkylene polyols or amine-terminated polytetramethylene glycols.

Suitable amines having three or more primary and/or secondary amino groups which are reactive toward a urea group are for example tris(aminoethyl)amine, tris(aminopropyl)amine, tris(aminoethyl)amine, trisaminohexane, 4-aminomethyl-1,8-octanediamine, trisaminononane, bis(aminoethyl)amine, bis(aminopropyl)amine,

bis(aminobutyl)amine, bis(aminopentyl)amine, bis(aminohexyl)amine, N-(2-aminoethyl)propanediamine, melamine, oligomeric diaminodiphenylmethanes (polymer MDA), N,N'-bis(3-aminopropyl)ethylenediamine, N,N'-bis(3-aminopropyl)butanediamine, N,N,N',N'-tetra(3-aminopropyl)ethylenediamine, N,N,N',N'-tetra(3-aminopropyl)butylenediamine, amine-terminated polyoxyalkylenepolyols with a functionality of three or more, polyethyleneimines with a functionality of three or more, or polypropyleneimines with a functionality of three or more.

Preferred amines having three or more reactive primary and/or secondary amino groups are tris(aminoethyl)amine, tris(aminopropyl)amine, tris(aminohexyl)amine, trisaminohexane, 4-aminomethyl-1,8-octanediamine, trisaminononane, bis(aminoethyl)amine, bis(aminopropyl)amine, bis(aminobutyl)amine, bis(aminopentyl)amine, bis(aminohexyl)amine, N-(2-aminoethyl)propanediamine, melamine or amine-terminated polyoxyalkylene polyols having a functionality of three or more.

Particular preference is given to amines having three or more primary amino groups, such as tris(aminoethyl)amine, tris(aminopropyl)amine, tris(aminohexyl)amine, trisaminohexane, 4-aminomethyl-1,8-octanediamine, trisaminononane or amine-terminated polyoxyalkylene polyols having a functionality of three or more:

It will be appreciated that mixtures of said amines can also be used.

In general amines having two primary or secondary amino groups as well as amines having three or more primary or secondary amino groups are used. Amine mixtures of this kind can also be characterized by the average amine functionality, with unreactive tertiary amino groups disregarded. Thus for example an equimolar mixture of a diamine and a triamine has an average functionality of 2.5. Preference is given to the reaction in accordance with the invention of amine mixtures in which the average amine functionality is from 2.1 to 10, in particular from 2.1 to 5.

The reaction of the urea with the diamine or polyamine to form the high-functionality highly branched polyurea of the invention is accompanied by elimination of ammonia, an alkylamine or dialkylamine or an arylamine or diarylamine. If one molecule of urea reacts with two amino groups then two molecules of ammonia or amine are eliminated if one molecule of urea reacts with only one amino group then a molecule of ammonia or amine is eliminated.

The reaction of the urea or ureas with the amine or amines can take place in a solvent. In that case it is possible in general to use any solvents which are inert toward the respective reactants. Preference is given to working in organic solvents, such as decane, dodecane, benzene, toluene, chlorobenzene, dichlorobenzene, xylene, dimethylformamide, dimethylacetamide or solvent naphtha.

In one preferred embodiment of the process of the invention the reaction is carried out in bulk, i.e., without inert solvent. The ammonia or amine liberated during the reaction between amine and urea can be separated off by distillation, where appropriate passing a gas over the liquid phase, passing a gas through the liquid phase, if appropriate under reduced pressure, and thus removed from the reaction equilibrium. This also accelerates the reaction.

In order to accelerate the reaction between amine and urea it is also possible to add catalysts or catalyst mixtures. Suitable catalysts are generally compounds which catalyze a formation of carbamate or urea, examples being alkali metal or alkaline earth metal hydroxides, alkali metal or alkaline earth metal hydrogen carbonates, alkali metal or alkaline earth metal carbonates, tertiary amines, ammonium compounds, or organic compounds of aluminum, tin, zinc, titanium, zirconium or bismuth. By way of example it is possible to use lithium, sodium, potassium or cesium hydroxide, lithium, sodium, potassium or cesium carbonate, lithium, sodium, potassium or cesium acetate, diazabicyclooctane (DABCO), diazabicyclononene (DBN), diazabicycloundecene (DBU), imidazoles, such as imidazole, 1-methylimidazole, 2-methylimidazole, and 1,2-dimethylimidazole, titanium tetrabutoxide, dibutyltin oxide, dibutyltin dilaurate, tin dioctoate, zirconium acetylacetonate or mixtures thereof.

The addition of the catalyst is made generally in an amount of from 50 to 10 000 ppm, preferably from 100 to 5000 ppm, by weight based on the amount of amine used.

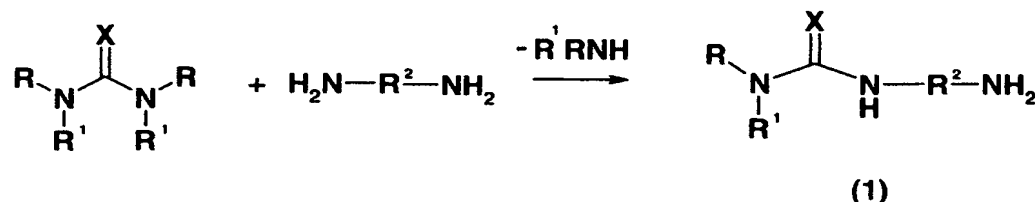
Following the reaction, in other words without further modification, the high-functionality highly branched polyureas prepared by the process of the invention are terminated with either amino groups or urea groups. They dissolve readily in polar solvents, such as in water and alcohols, such as methanol, ethanol, butanol or alcohol/water mixtures, dimethylformamide, dimethylacetamide, N-methylpyrrolidone, ethylene carbonate or propylene carbonate.

- A high-functionality polyurea for the purposes of the invention is a product which has at least three, preferably at least six, in particular at least ten urea groups or other functional groups. There is in principle no upper limit on the number of functional groups, although products with a very large number of functional groups may exhibit unwanted properties, such as a high viscosity or a poor solubility. The high-functionality polyureas of the present invention generally do not have more than 200 functional groups, preferably not more than 100 functional groups. By functional groups here are meant primary, secondary or tertiary amino groups or urea groups. In addition it is possible for the high-functionality highly branched polyurea to contain further functional groups, which do not participate in the synthesis of the highly branched polymer (see below). These additional functional groups can be introduced by means of diamines or polyamines which contain further functional groups in addition to primary and secondary amino groups.
- 15 In the test below the synthesis of the novel high-functionality highly branched polyureas is illustrated in principle.

- In the case of the preparation of the high-functionality polyureas the ratio of amines having at least two amino groups which are reactive with urea groups to the urea can be set so that the resultant most simple condensation product (referred to below as condensation product (A)) contains on average either one urea group and more than one amino group which is reactive with the urea group or else contains one amino group which is reactive with urea groups, and more than one urea group. The simplest structure arising for the condensation product (A) of a urea and a diamine or polyamine comprises the arrangements  $XY_n$  or  $X_nY$ , where  $n$  is generally a number between 1 and 6, preferably between 1 and 4, more preferably between 1 and 3.  $X$  denotes a urea group,  $Y$  an amino group reactive therewith. The reactive group, which in this case is present as a single group, is referred to in the text below as "focal group".
- 30 If, for example, in the preparation of the simplest condensation product (A) from a urea and a difunctional primary amine the molar ratio is 1:1, then the result on average is a molecule of type  $XY$ , illustrated by the general formula 1.



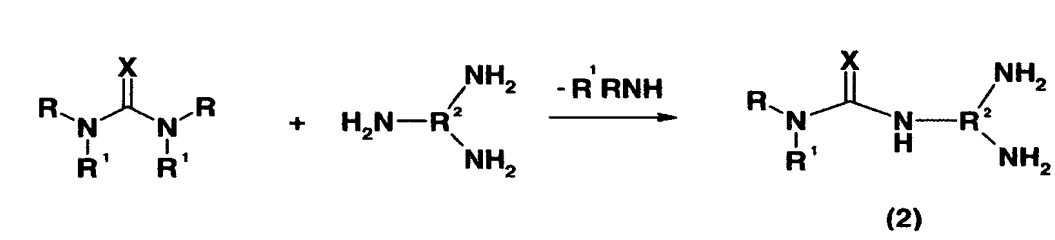
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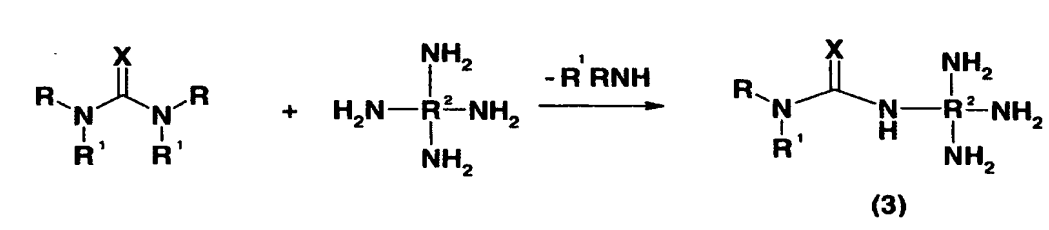
5 X here can be oxygen or sulfur, R and R<sup>1</sup>, independently of one another, can be hydrogen or any desired aliphatic, aromatic or araliphatic radicals and R<sup>2</sup> can be any desired aliphatic, aromatic or araliphatic radicals.

The preparation of the condensation product (A) from a urea and a trifunctional amine at a molar ratio of 1:1 results on average in a molecule of type XY<sub>2</sub>, illustrated by the general formula 2. The focal group in this case is a urea group.

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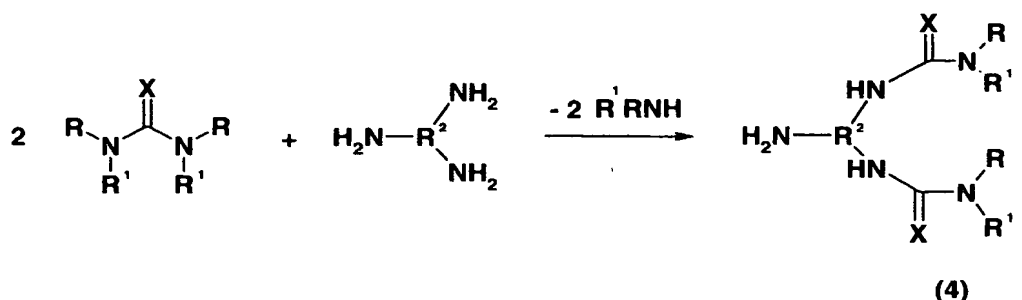


15 In the preparation of the condensation product (A) from a urea and a tetrafunctional amine, again with the molar ratio at 1:1, the result is on average a molecule of type XY<sub>3</sub>, illustrated by the general formula 3. The focal group in this case is again a urea group.

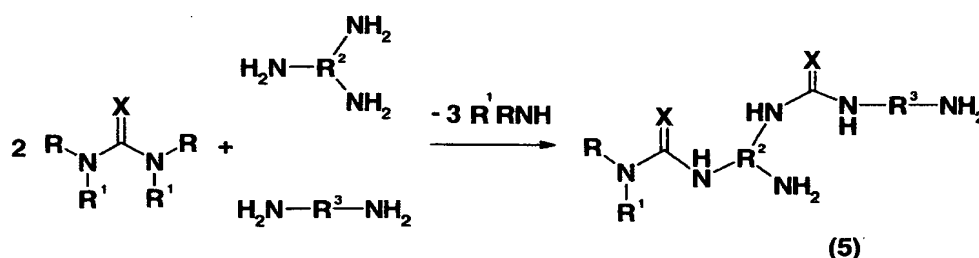


20 If a urea is reacted with a triamine and the molar ratio of urea to triamine is 2:1, the result is on average a simplest condensation product (A) of type X<sub>2</sub>Y, which is illustrated by the general formula 4. The focal group in this case is an amino group.

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If difunctional compounds are additionally added to the components, such as a urea or a diamine, for example, the effect of this is to increase the length of the chains, as illustrated for example in formula 5. The result is again on average a molecule of type  $\text{XY}_2$ ; the focal group is a urea group.



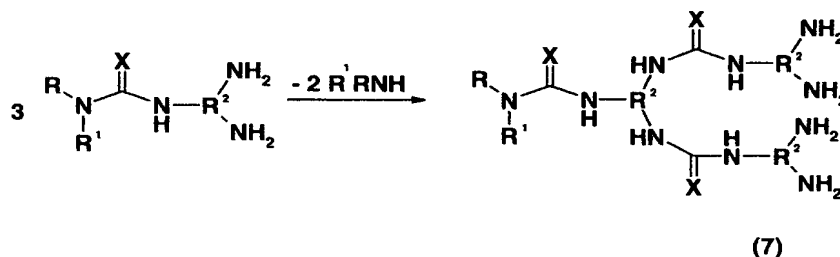
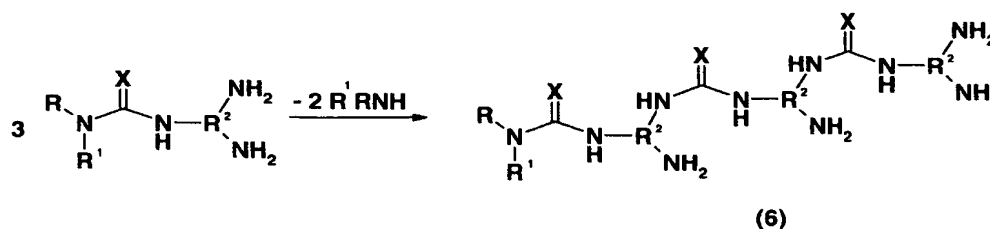
X here can be oxygen or sulfur, R and  $\text{R}'$ , independently of one another, can be hydrogen or any desired aliphatic, aromatic or araliphatic radicals and  $\text{R}^2$  and  $\text{R}^3$  can be any desired aliphatic, aromatic or araliphatic radicals.

The simple condensation products (A) described by way of example in formulae 1 - 5 react intermolecularly to form high-functionality polycondensation products, called polycondensation products (P) below. The reaction to the condensation product (A) and to the polycondensation product (P) takes place normally at a temperature of from 0 to 250°C, preferably at from 60 to 180°C, without solvent or in solution.

In view of the nature of the condensation products (A) it is possible that the condensation reaction may result in polycondensation products (P) having a variety of structures which contain branching but no crosslinking. Furthermore, the polycondensation products (P) contain either on average a urea focal group and more than two amines which are reactive with urea groups, or else contain on average as focal group an amine which is reactive with urea groups, and more than two urea

groups. The number of reactive groups is a function of the nature of the condensation products (A) employed and of the degree of polycondensation.

- For example, a condensation product (A) may react in accordance with the general formula 2 by threefold intermolecular condensation to form two different polycondensation products (P), which are reproduced in the general formulae 6 and 7.



- For terminating the intermolecular polycondensation reaction there are a variety of options. For example, the temperature can be lowered to a range within which the reaction comes to a standstill and the product (A) or the polycondensation product (P) is storage-stable.
- In a further embodiment it is possible to terminate the reaction by adding a product containing groups reactive toward the focal group of (P) to the product (P) as soon as, by virtue of the intermolecular reaction of the condensation product (A), a polycondensation product (P) is present which has the desired degree of polycondensation. Thus in the case where the focal group is a urea group a monoamine, diamine or polyamine can be added, for example. In the case of an amine focal group a mono-, di- or polyurethane, a mono-, di- or polyisocyanate, an aldehyde, a ketone or an acid derivative which is reactive with amine can be added to the product (P).

Additionally it is also possible to control the intermolecular polycondensation reaction either by adding the appropriate catalyst or by choosing a suitable temperature. Moreover, the average molecular weight of the polymer (P) can be adjusted by way of the composition of the starting components and by way of the residence time. The  
5 condensation products (A) and the polycondensation products (P) which were prepared at elevated temperature are normally stable over a relatively long period of time at room temperature.

The preparation of the high-functionality highly branched polyureas of the invention  
10 takes place in general within a pressure range from 0.1 mbar to 20 bar, preferably from 3 mbar to 3 bar, in reactors or reactor cascades which are operated batchwise, semicontinuously or continuously.

As a result of the aforementioned setting of the reaction conditions and, where  
15 appropriate, the choice of appropriate solvent it is possible for the products of the invention to be processed further following their preparation, without additional purification.

In another preferred embodiment the polyureas of the invention may contain other  
20 functional groups. Functionalization can in that case be effected during the reaction of the urea with the amine or amines, in other words during the polycondensation reaction which produces the increase in molecular weight, or else after the end of the polycondensation reaction, by subsequent functionalization of the resulting polyureas.

25 If before or during the molecular weight build-up components are added which as well as amino groups or urea groups contain further functional groups, then the product is a polyurea having randomly distributed further - that is, other than the urea groups or amino groups - functional groups.

30 By way of example, before or during the polycondensation, components can be added which in addition to amino groups or urea groups contain hydroxyl groups, mercapto groups, tertiary amino groups, ether groups, carboxyl groups, sulfonic acid groups, phosphonic acid groups, silane groups, siloxane groups, aryl radicals or short- or long-chain alkyl radicals.

35 Hydroxyl-containing components which can be added to the functionalization include for example ethanolamine, N-methylethanolamine, propanolamine, isopropanolamine,

butanolamine, 2-amino-1-butanol, 2-(butylamino)ethanol, 2-(cyclohexylamino)ethanol, 2-(2'-aminoethoxy)ethanol or higher alkoxylation products of ammonia, 4-hydroxypiperidine, 1-hydroxyethylpiperazine, diethanolamine, dipropanolamine, diisopropanolamine, tris(hydroxymethyl)aminomethane or tris(hydroxyethyl)amino-  
5 methane.

Mercapto-containing components which can be used for functionalization include, for example cysteamine. With tertiary amino groups it is possible to functionalize the highly branched polyureas through the use, for example, of di(aminoethyl)methylamine, di(aminopropyl)methylamine or N,N-dimethylethylenediamine. With ether groups it is  
10 possible to functionalize the highly branched polyureas by using amine-terminated polyetherols (known as Jeffamines). With acid groups it is possible to functionalize the highly branched polyureas through the use, for example, of aminocarboxylic acids, aminosulfonic acids or aminophosphonic acids. With groups containing silicon it is  
15 possible to functionalize the highly branched polyureas through the use of hexamethyldisilazane. With long-chain alkyl radicals the highly branched polyureas can be functionalized by using alkylamines or alkylisocyanates having long-chain alkyl radicals.

20 The polyureas can also be functionalized, furthermore, by using small amounts of monomers which contain functional groups different from amino groups or urea groups. Mention may be made here by way of example of alcohols with a functionality of two, three or more, which can be incorporated into the polyurea by way of carbonate or carbamate functions. Thus, for example, hydrophobic properties can be obtained by  
25 adding long-chain alkanediols, while polyethylene oxide diols or triols produce hydrophilic properties in the polyurea.

The said functional groups other than amine or urea groups which are introduced before or during the polycondensation are generally introduced in amounts of from 0.1  
30 to 80 mol%, preferably in amounts of from 1 to 50 mol%, based on the sum of the amino and urea groups.

Subsequent functionalization of high-functionality highly branched polyureas containing amino groups can be achieved for example by adding molecules containing acid  
35 groups, isocyanate groups, keto groups or aldehyde groups or molecules containing activated double bonds, acrylic double bonds for example. By way of example it is

possible to obtain polyureas containing acid groups by reaction with acrylic acid or maleic acid and derivatives thereof, with subsequent hydrolysis if desired.

5 Additionally it is possible to convert high-functionality polyureas containing amino groups into high-functionality polyurea polyols by reaction with alkylene oxides, for example ethylene oxide, propylene oxide or butylene oxide.

10 A further possibility of preparing polyurea/polyether compounds lies in the reaction of the polyureas with amino-terminated polyalkylene oxides having a functionality of one, two or more, preferably polyethylene oxides, polypropylene oxides or polyethylene-propylene oxides.

15 The formation of salts with protic acids or quaternization of the amino functions with alkylating reagents, such as methyl halides or dialkyl sulfates, allows the high-functionality, highly branched polyureas to be adjusted water-solubly or water-emulsifiably.

20 In order to achieve hydrophobicization it is possible for amine-terminated high-functionality highly branched polyureas to be reacted with saturated or unsaturated long-chain carboxylic acids, their derivatives that are reactive toward amine groups, or else aliphatic or aromatic isocyanates.

Polyureas terminated with urea groups can be obtained by reaction with long-chain alkyl amines or long-chain aliphatic monoalcohols.

25 A great advantage of the process of the invention is its economy. Not only the reaction to form the polycondensate (A) or polycondensation product (P) but also the reaction of (A) or (P) to form polyureas with further functional groups can take place in one reaction apparatus, which is an advantage both technically and economically.

30 The present invention also provides for the use of the high-functionality highly branched polyureas of the invention as adhesion promoters and thixotropic agents, solubilizers, surface modifiers and as components for producing paints and varnishes, coatings, adhesives, sealants, anticorrosion agents, castable elastomers, and foams.

35 The present invention is illustrated by the following examples:

### Examples

## Preparation of the polyureas according to the invention

Examples 1-8, general procedure:

5

The amine or amine mixture, the urea and potassium carbonate as catalyst were charged in accordance with the information in table 1 to a three-neck flask equipped with stirrer, reflux condenser and internal thermometer, and the initial charge was heated. Evolution of gas commenced at 100-110°C. The reaction mixture was stirred at the stated temperatures for the time indicated in table 1 and thereafter the reaction mixture was cooled to room temperature.

10

Example 9:

15 103 g of diethylenetriamine and 1.4 g of potassium carbonate were charged to a three-necked flask equipped with stirrer, reflux condenser and internal thermometer and the initial charge was heated to 150°C. Then, at this temperature, 60 g of urea, likewise heated to 150°C, were added from a heatable feed vessel over the course of 30 minutes. Gas evolution commenced immediately after the beginning of the feed. After the end of the feed the reaction mixture was stirred at 150°C for 6 h more and thereafter was cooled to room temperature.

20

Analysis of the polyureas of the invention:

25 The polyureas obtained according to examples 1 to 9 were analyzed by gel permeation chromatography using a refractometer as detector. The mobile phase was hexafluoroisopropanol, with polymethyl methacrylate (PMMA) being used as the standard for determining the molecular weight.

The glass transition temperatures were determined by means of differential scanning calorimetry (DSC), evaluation taking place on the basis of the second heating curve.

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The results of the analyses are collated in table 2.

Table 1

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Example No.	Amine	Urea	Molar ratio of	Potassium carbonate (% by	Reaction time and reaction
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			amine:ur ea	weight based on amine)	temperature
1	TAEA	HS	1:1	0.14	4 h at 150°C
2	DPTA	HS	1:1	0.11	4.5 h at 140°C + 3.5 h at 150°C
3	DPTA	HS	1:1.5	0.25	2 h at 120°C
4	TAEA	HS	1:2	0.17	1 h at 120°C + 1 h at 130°C
5	TAEA	DMHS	1:1	0.17	7.5 h at 130°C + 2 h at 140°C
6	TAEA	DMHS	1:2	0.25	1.5 h at 120°C + 2 h at 130°C + 2 h at 140°C
7	TAEA/HDA molar 1:1	HS	1:1	0.14	2 h at 120°C + 2 h at 130°C + 1 h at 140°C
8	TAEA/IPDA molar 1:1	HS	1:1	0.15	2.5 h at 120°C + 1 h at 130°C

TAEA: Tris(aminoethyl)amine

DETA: Diethylenetriamine

DPTA; dipropylenetriamine

5 HDA: Hexamethylenediamine

IPDA: Isophorondiamine

HS: Urea

DMHS: N,N'-dimethylurea

10 Table 2

Example No.	Molar mass (Mn)	Molar mass (Mw)	Glass transition temperature Tg (°C)
1	3900	10000	-1.5
2	1950	2600	19
3	1800	2100	16
4	2300	3100	16



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5	3100	5100	-28
6	4000	6700	-18
7	3100	5800	69
8	1800	2800	15
9	1800	2400	22